

Relativistic separable dual-space Gaussian Pseudopotentials from H to Rn

C. Hartwigsen, S. Goedecker, J. Hutter
 Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

We generalize the concept of separable dual-space Gaussian pseudopotentials to the relativistic case. This allows us to construct this type of pseudopotential for the whole periodic table and we present a complete table of pseudopotential parameters for all the elements from H to Rn. The relativistic version of this pseudopotential retains all the advantages of its nonrelativistic version. It is separable by construction, it is optimal for integration on a real space grid, it is highly accurate and due to its analytic form it can be specified by a very small number of parameters. The accuracy of the pseudopotential is illustrated by an extensive series of molecular calculations.

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I. INTRODUCTION

Pseudopotentials are a well established tool in ab initio structure calculations of molecules and solids. First, by replacing the atom by a pseudo atom the number of orbitals which have to be calculated is reduced and second, the size of the basis set can substantially be reduced because the pseudo wave functions are smoother than their all-electron counterparts. In addition relativistic effects which are relevant for heavier elements can be included in the pseudopotential construction so that a non-relativistic calculation can reproduce these

In 1982 Bachelet, Hamann and Schlüter¹ published a list of pseudopotentials for all elements up to Pu, that has found widespread application. There have been many attempts to improve the pseudopotential transferability and their numerical efficiency since. One major advance was the introduction of a separable form by Kleinmann and Bylander², that significantly reduces the computational effort for the calculation of the nonlocal part especially when using a plane wave basis set. Gonze, Stumpf and Scheffler³ investigated the Kleinmann-Bylander form carefully and published a list⁴ of pseudopotentials for many elements up to Xe. Goedecker *et al.*⁵ proposed a new dual-space Gaussian type pseudopotential which is separable and satisfies an optimality criterion for the real space integration of the nonlocal part. For large systems there is only a quadratic scaling with respect to the system size if the integration of the nonlocal part is performed on a real space grid compared to a cubic scaling if a Fourier space integration is used⁶. In contrast to most other pseudopotential construction methods Goedecker *et al.* also included unoccupied orbitals

in their method thereby generating highly transferable pseudopotentials. Goedecker *et al.* gave the non relativistic pseudopotential parameters for the first two rows of the periodic system and showed that their pseudopotentials give highly accurate results in molecular calculations. They obtained results which are much closer to the quasi-exact all-electron LDA^{11,12} (local density approximation) value than what is obtained in all-electron calculations with a standard Gaussian 6-31G* basis sets. With other words the errors due to the pseudopotential approximation were much smaller than the errors in a all-electron calculation introduced by incomplete basis sets.

In this paper we give the parameters of dual-space Gaussian pseudopotentials for all elements from H to Rn. In contrast to Goedecker *et al.* all pseudopotentials are now generated on the basis of a fully relativistic all-electron calculation, i.e. by solving the two component Dirac equation. The generalization of the norm-conservation property to the relativistic case proposed by Bachelet and Schlüter¹⁶ is used for the construction. We also introduced some slight modifications of the analytic form of the pseudopotential. The parameters are given in the context of the local density approximation. Even though the parameters change only slightly if the pseudopotential is constructed within the framework of a generalized gradient approximation^{14,15} (GGA) functional, we found that molecular properties are less accurately described if LDA pseudopotentials are inserted in a molecular calculation using GGA's. Since it is not possible to construct pseudopotentials tables for all current GGA schemes, a program that can construct pseudopotentials for the most common GGAs can be obtained from the authors.

II. FORM OF THE PSEUDOPOTENTIAL

The local part of the pseudopotential is given by

$$V_{\text{loc}}(r) = \frac{-Z_{\text{ion}}}{r} \text{erf}\left(\frac{r}{\sqrt{2}r_{\text{loc}}}\right) + \exp\left[-\frac{1}{2}\left(\frac{r}{r_{\text{loc}}}\right)^2\right] \times \left[C_1 + C_2\left(\frac{r}{r_{\text{loc}}}\right)^2 + C_3\left(\frac{r}{r_{\text{loc}}}\right)^4 + C_4\left(\frac{r}{r_{\text{loc}}}\right)^6\right] \quad (1)$$

where erf denotes the error function. Z_{ion} is the ionic charge of the atomic core, i.e. the total charge minus the charge of the valence electrons. The nonlocal contribution $V_l(\mathbf{r}, \mathbf{r}')$ to the pseudopotential is a sum of separable terms

$$V_l(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{r}}) p_i^l(r) h_{i,j}^l p_j^l(r') Y_{l,m}^*(\hat{\mathbf{r}}') \quad (2)$$

where $Y_{l,m}$ are the spherical harmonics and l the angular momentum quantum number. The projectors $p_i^l(r)$ are Gaussians of the form

$$p_i^l(r) = \frac{\sqrt{2} r^{l+2(i-1)} \exp\left(-\frac{r^2}{2r_i^2}\right)}{r_i^{l+(4i-1)/2} \sqrt{\Gamma(l + \frac{4i-1}{2})}} \quad (3)$$

where Γ denotes the gamma function. The projectors satisfy the normalisation condition

$$\int_0^\infty p_i^l(r) p_i^l(r) r^2 dr = 1. \quad (4)$$

It is a special property of our pseudopotential that it has also an analytical form if expressed in reciprocal space. The Fourier transform of the pseudopotential is given by

$$\begin{aligned} V_{\text{loc}}(g) = & -\frac{4\pi Z_{\text{ion}}}{\Omega g^2} e^{-\frac{(gr_{\text{loc}})^2}{2}} \\ & + \sqrt{8\pi^3} \frac{r_{\text{loc}}^3}{\Omega} e^{-\frac{(gr_{\text{loc}})^2}{2}} \times \{ C_1 + C_2 (3 - g^2 r_{\text{loc}}^2) \\ & + C_3 (15 - 10(gr_{\text{loc}})^2 + (gr_{\text{loc}})^4) + C_4 (105 \\ & - 105(gr_{\text{loc}})^2 + 21(gr_{\text{loc}})^4 - (gr_{\text{loc}})^6) \} \end{aligned} \quad (5)$$

for the local part and

$$V_l(\mathbf{g}, \mathbf{g}') = (-1)^l \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{g}}) p_i^l(g) \times h_{i,j}^l p_j^l(g') Y_{l,m}^*(\hat{\mathbf{g}}') \quad (6)$$

for the nonlocal part. The Fourier transform of the projectors $p_i^l(r)$ can be calculated analytically and for the relevant cases one obtains

$$p_1^{l=0}(g) = \frac{4\sqrt{2r_0^3}\pi^{5/4}}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (7)$$

$$p_2^{l=0}(g) = \frac{8\sqrt{\frac{2r_0^3}{15}}\pi^{5/4}(3 - g^2 r_0^2)}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (8)$$

$$p_3^{l=0}(g) = \frac{16\sqrt{\frac{2r_0^3}{105}}\pi^{5/4}(15 - 10g^2 r_0^2 + g^4 r_0^4)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_0)^2]}, \quad (9)$$

$$p_1^{l=1}(g) = \frac{8\sqrt{\frac{r_1^5}{3}}\pi^{5/4}g}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (10)$$

$$p_2^{l=1}(g) = \frac{16\sqrt{\frac{r_1^5}{105}}\pi^{5/4}g(5 - g^2 r_1^2)}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (11)$$

$$p_3^{l=1}(g) = \frac{32\sqrt{\frac{r_1^5}{1155}}\pi^{5/4}g(35 - 14g^2 r_1^2 + g^4 r_1^4)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_1)^2]}, \quad (12)$$

$$p_1^{l=2}(g) = \frac{8\sqrt{\frac{2r_2^7}{15}}\pi^{5/4}g^2}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_2)^2]}, \quad (13)$$

$$p_2^{l=2}(g) = \frac{16\sqrt{\frac{2r_2^7}{105}}\pi^{5/4}g^2(7 - g^2 r_2^2)}{3\sqrt{\Omega} \exp[\frac{1}{2}(gr_2)^2]}, \quad (14)$$

$$p_1^{l=3}(g) = \frac{16\sqrt{\frac{r_3^9}{105}}\pi^{5/4}g^3}{\sqrt{\Omega} \exp[\frac{1}{2}(gr_3)^2]}. \quad (15)$$

In both real and Fourier space the projectors have the form of a Gaussian multiplied by a polynomial. Due to this property the dual-space Gaussian pseudopotential is the optimal compromise between good convergence properties in real and Fourier space. The multiplication of the wave function with the nonlocal pseudopotential arising from an atom can be limited to a small region around the atom as the radial projectors $p_i^l(r)$ asymptotically tend to zero outside the covalent radius of the atom. In addition, a very dense integration grid is not required as the nonlocal pseudopotential is reasonably smooth because of its good decay properties in Fourier space.

The use of this form for the pseudopotential is also very advantageous if atom centered basis functions are used instead of plane waves. Because of the separability all three-center integrals are products of two-center integrals and so only these two-center integrals have to be calculated. If atom centered Gaussian type orbitals are used, these two-center integrals can easily be evaluated analytically.

In the relativistic case the spin orbit coupling splits up all orbitals with $l > 0$ into a spin up and spin down orbital with overall angular momentum $j = l \pm 1/2$. So for each angular-momentum $l > 0$ one spin up and spin down orbital with different wave functions and pseudopotentials exist. Following Bachelet and Schlüter¹⁶ we give a weighted average and difference potential of these potentials. The average pseudopotential is conveniently defined as

$$V_l(\mathbf{r}, \mathbf{r}') = \frac{1}{2l+1} (lV_{l-1/2}(\mathbf{r}, \mathbf{r}') + (l+1)V_{l+1/2}(\mathbf{r}, \mathbf{r}')) \quad (16)$$

weighted by the different j degeneracies of the $l \pm 1/2$ orbitals. The difference potential describes the spin orbit coupling and is defined as

$$\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') = \frac{2}{2l+1} (V_{l+1/2}(\mathbf{r}, \mathbf{r}') - V_{l-1/2}(\mathbf{r}, \mathbf{r}')). \quad (17)$$

The total pseudopotential is then given by

$$V(\mathbf{r}, \mathbf{r}') = V_{\text{loc}}(r)\delta(\mathbf{r} - \mathbf{r}') + \sum_l V_l(\mathbf{r}, \mathbf{r}') + \Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') \mathbf{L} \cdot \mathbf{S}. \quad (18)$$

where $V_{\text{loc}}(r)$ and $V_l(\mathbf{r}, \mathbf{r}')$ are now scalar relativistic quantities but with the same form (eq.(1,2)) as the non-relativistic case. To express $\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}')$ we also use eq.(2) just replacing the $h_{i,j}^l$ by different parameters $k_{i,j}^l$, i.e.

$$\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^3 \sum_{j=1}^3 \sum_{m=-l}^{+l} Y_{l,m}(\hat{\mathbf{r}}) p_i^l(r) k_{i,j}^l p_j^l(r') Y_{l,m}^*(\hat{\mathbf{r}}'). \quad (19)$$

Neglecting the contributions from $\Delta V_l^{\text{SO}}(\mathbf{r}, \mathbf{r}')$ in eq.(18) gives the average potential that contains all scalar parts of the relativistic pseudopotential whereas the total potential contains relativistic effects up to order α^2 .

III. DETERMINATION OF THE PSEUDOPOTENTIAL PARAMETERS

The parameters of the pseudopotentials were found by minimising the differences between the eigenvalues and the charges within an atomic sphere of the all-electron and the pseudo atom. In most cases the radius of the atomic sphere was taken to be the covalent radius of the atom. For consistency we always performed a fully relativistic calculation for the all-electron atom even when relativistic effects are negligible. The exchange and correlation energy was calculated with the functional given by Goedecker *et al.*⁵ This functional reproduces very well the Perdew-Wang¹⁷ 1992 but is much easier to compute. To ensure transferability of the pseudopotential we also considered the next two or three higher unoccupied orbitals for each angular-momentum and the lowest orbital of the next two unoccupied angular-momentum. However in our calculations we never exceeded $l_{\text{max}}=3$. The atom was put in an external parabolic confining potential to have well defined unoccupied orbitals. The pseudopotential parameters given in table I typically reproduce the eigenvalues of the occupied orbitals with an error of less than 10^{-5} a.u. and for the unoccupied orbitals to within 10^{-3} a.u. Pseudopotentials containing semi-core electrons (next Sec.) are an exception as the errors for the semi-core orbitals are usually larger than for the valence orbitals. In many cases we found it unnecessary to include all unoccupied orbitals in our fitting procedure. For most cases the inclusion of only the first unoccupied orbital for an angular-momentum results in comparable good results for the following higher unoccupied orbitals. Nevertheless we always checked all-electron and pseudo eigenvalues and charges of the unoccupied orbitals to verify this.

It has already been discussed by Goedecker *et al.* that our fitting procedure yields pseudopotentials that obey

the norm-conservation⁷ condition and meet several additional conditions^{8–10}, such as extended norm conservation and hardness, thereby leading to pseudopotentials of a very high quality.

In table III we give the transferability errors for several excited and ionized states for some elements.

The construction of our pseudopotential differs somehow from the usual method because we fit the pseudopotential parameters that give the best overall representation for the eigenvalues and charges of several orbitals rather than producing pseudo wave functions that are identical to their all-electron counterparts beyond some cutoff radius. Therefore the wave functions of the pseudo atom and all-electron atom approach each other only exponentially. Nevertheless the difference is very small beyond the core region as can be seen from Fig. 1. A second consequence of our fitting procedure is that contrary to most other pseudopotential construction methods the local part of our pseudopotential does not correspond to a certain wave function.

It is a special feature of our method that we fit our parameters directly against the all-electron eigenvalues and charges rather than fitting analytical or numerical potentials that reproduce pseudo wave functions which themselves are constructed from their all-electron counterparts. Therefore our pseudopotentials require significantly fewer parameters than those tabulated by Bachelet, Hamann and Schlüter¹. During the generation of our pseudopotentials we found that there is in general no single minimal parameter set that gives the best overall pseudopotential for one atom. This finding is different to the former study of Goedecker *et al.* where only the first two rows of the periodic table have been considered. We always tried to use the minimum parameter set which is sufficient to reproduce the desired accuracy of the fitted eigenvalues and charges. Identical parameter sets were used for comparable elements, i.e. the same parameter set was used for all 3d-elements or the 4d-elements, respectively. The fitting of the pseudopotential parameters is numerically demanding as many local minima exist so that sometimes up to some 10^5 pseudopotential evaluations are necessary until one finds good parameter values. We used a slow Simplex-Downhill algorithm¹⁸ for the optimisation that proved to be much more robust than more sophisticated methods. The pseudopotential parameter r_{loc} was set by hand except for the first row because this parameter is not easily accessible by our fitting procedure. For many elements we generated and tested pseudopotentials with different values of r_{loc} . After selection of the optimum pseudopotentials the r_{loc} values for the elements in between were interpolated so that no discontinuities occur.

IV. SEMI-CORE ELECTRONS

For many atoms there is no unambiguous separation of the electronic system into a well isolated core and valence shell. For example it is well known the $(n-1)p$ -levels of the the heavy alkali atoms are relatively shallow in energy and extended in space. The $3d$ -wave functions of the $3d$ -elements are strongly localized so that there is a significant overlap with the $3(s,p)$ -wave functions although the later are much lower in energy than the $3d$ - and $4(s,p)$ -valence wave functions. The same is true for the $4d$ - and $5d$ -elements. Analogous the $4f$ -wave functions of the $4f$ -elements are so localized that they overlap with the $5s$ - and $5p$ -wave functions. In all these cases where a non negligible overlap between valence and core wave functions exists the frozen-core approximation underlying the construction of all pseudopotentials is not well satisfied. One way to overcome this problem is the inclusion of a nonlinear core correction¹⁹ that considers the contribution of the core charge to the exchange-correlation potential. The other more straight forward solution is the explicit inclusion of the semi-core electrons into the pseudopotential. In this work we decided for the second method. This ensures that our semi-core pseudopotentials still can be used with programs where non linear corrections are not considered. In addition the explicit inclusion of the semi-core electrons ensures that our pseudopotentials still work well for systems where non linear core corrections fail. It is unnecessary that the eigenvalues and charge distribution of the semi-core wave functions have the same accuracy as the valence wave functions of the pseudo atom. We always tried to generate semi-core pseudopotentials with semi-core pseudo wave functions that are as smooth as possible but still yield accurate results for the valence wave functions. Therefore the error for the eigenvalues of semi-core wave functions for our pseudopotentials is within 10^{-3} to 10^{-2} a.u. which is about 3 orders of magnitude worse than the typically error for the valence wave functions.

The choice which electrons are treated as semi-core electrons also depends on the required accuracy. As we were interested to generate pseudopotentials that can be used together with plane wave basis sets within a reasonable computational effort we tried to include not too many semi-core electrons into our pseudopotentials. Our semi-core pseudopotentials for the group Ia and IIa elements, the transition metals of group IIIb to VIIIB and the lanthanides trade the $(n-1)s$ - and the $(n-1)p$ -electrons as semi-core electrons. For the elements of group Ib, IIb and IIIa (except B and Al) all electrons of the completely filled nd -shell are treated as semi-core electrons.

For all elements mentioned above semi-core wave functions improve the description of highly positive charged ions. In table III the transferability error of two Ti pseudopotentials is listed for several states. For most states the calculated excitation energies are much closer to the all-electron values for the Ti semi-core pseudopotential

including the $3s$ - and $3p$ -semi-core electrons. This is most significant for the $4s^04p^03d^0$ state which corresponds to a Ti^{4+} -ion. For the $4e$ -pseudopotential the error is 0.1 Hartree but only 0.28×10^{-2} Hartree for the $12e$ -semi-core pseudopotential.

Pseudopotentials with semi-core wave functions always require higher computational effort. They contain more electrons and larger basis sets are necessary for a sufficient description of the localized semi-core wave functions. In many applications like molecular structure calculation semi-core pseudopotentials yield converged results with comparable small basis sets even if the calculated total energy is still far from its converged value. Therefore the inclusion of semi-core electrons not inevitably requires the use of extremely large basis sets. In fact in our molecular calculations the highest plane wave energy cutoff were needed for calculations with the fluorine pseudopotential which has no semi-core electrons at all.

In many cases it is not quite clear, if semi-core electrons play an important role or not. For most applications the need to use semi-core pseudopotentials depends on the required accuracy and necessary computational effort and should be tested carefully. Therefore we constructed both type of pseudopotentials for most elements where semi-core electrons can play a significant role in electronic structure calculations.

V. MOLECULES

We tested our pseudopotentials by calculating the bond lengths of a large number of molecules. In all calculations we used our scalar relativistic pseudopotentials neglecting the terms for spin orbit interaction. Whenever possible we tried to determine values for the bond lengths, that are converged to $\approx 10^{-3}$ Bohr. To obtain this high level of accuracy extremely large boxes and high plane wave energy cutoffs were needed so that for some molecules the accuracy of the calculations was limited by our computational resources. The calculated bond lengths together with their experimental values are listed in table II. As a reference for the quasi-exact LDA value we also list the bond lengths calculated with GAUSSIAN 94²⁰ using a 6-311G++(3df,3pd) basis set (for the $3d$ -elements no f -polarization functions have been used). With a few exceptions the values calculated with GAUSSIAN 94 agree within a few thousands of a Bohr with the LDA results published by Dickson and Becke²¹ and therefore should be close to the LDA limit. For some molecules where no high precision basis sets are available we took the all-electron results from Dickson and Becke. To estimate the error arising from the pseudopotential approximation our calculated values should be compared with these LDA results rather than with the experimental bond lengths. Unfortunately exact LDA values for molecules containing heavier elements often are not avail-

able because of the lack of a sufficiently accurate basis set.

The bond lengths calculated with our pseudopotentials, including semi-core electrons where necessary, agree very well with the all-electron values obtained with GAUSSIAN 94. The error of the pseudopotential approximation for first row atoms is nearly ten times smaller than the LDA error and for the heavier elements at least comparable to the LDA error. In all cases except for the non semi-core pseudopotentials the accuracy relative to the exact LDA value is, however, better than the results obtained with standard Gaussian 6-31G* basis sets and it is comparable or better than the results obtained with other all-electron methods. It must be mentioned that our results especially for molecules with heavier elements are not exactly comparable to the values obtained with GAUSSIAN 94 or the values of Dickson and Becke as our pseudopotentials also include relativistic effects.

For some non semi-core pseudopotentials the error in the calculated bond lengths is quite large. Nevertheless these pseudopotentials may still be of interest for electronic structure calculations if no high precision is required or the computational resources are limited. These pseudopotentials require only small basis sets which is sometimes a necessity for the study of large systems.

Our calculated bond lengths containing only first or second row atoms also agree to within one or two thousands of a Bohr to those obtained with nonrelativistic versions of these pseudopotentials that have already been published⁵ (differences in the case of HCN are due to the choice of a different simulation box). This clearly demonstrates that relativistic effects do not influence the bond lengths for these molecules on a relevant scale.

VI. THE PARAMETERS

In the following we list the parameters for all elements up to Rn. The entries in Table I have the following meaning:

Element	Z_{ion}	r_{loc}	C_1	C_2	C_3	C_4
		r_0	$h_{1,1}^0$	$h_{2,2}^0$	$h_{3,3}^0$	
		r_1	$h_{1,1}^1$	$h_{2,2}^1$	$h_{3,3}^1$	
			$k_{1,1}^1$	$k_{2,2}^1$	$k_{3,3}^1$	
		r_2	$h_{1,1}^2$	$h_{2,2}^2$	$h_{3,3}^2$	
			$k_{1,1}^2$	$k_{2,2}^2$	$k_{3,3}^2$	
		\vdots				.

Only the nonzero parameters are shown in table I. Parameters for elements marked with ^{sc} correspond to semi-core pseudopotentials. In order to keep the table as small as possible the coefficients $h_{i,j}^l$ and $k_{i,j}^l$ of the nonlocal projectors for $i \neq j$ are not listed. To get the full parameter set the missing $h_{i,j}^l$ and $k_{i,j}^l$ have to be calculated from the $h_{i,i}^l$ and $k_{i,i}^l$. The relevant equations for the $h_{i,j}^l$ are:

$$h_{1,2}^0 = -\frac{1}{2}\sqrt{\frac{3}{5}}h_{2,2}^0, \quad (20)$$

$$h_{1,3}^0 = \frac{1}{2}\sqrt{\frac{5}{21}}h_{3,3}^0, \quad (21)$$

$$h_{2,3}^0 = -\frac{1}{2}\sqrt{\frac{100}{63}}h_{3,3}^0, \quad (22)$$

$$h_{1,2}^1 = -\frac{1}{2}\sqrt{\frac{5}{7}}h_{2,2}^1, \quad (23)$$

$$h_{1,3}^1 = \frac{1}{6}\sqrt{\frac{35}{11}}h_{3,3}^1, \quad (24)$$

$$h_{2,3}^1 = -\frac{1}{6}\frac{14}{\sqrt{11}}h_{3,3}^1, \quad (25)$$

$$h_{1,2}^2 = -\frac{1}{2}\sqrt{\frac{7}{9}}h_{2,2}^2, \quad (26)$$

$$h_{1,3}^2 = \frac{1}{2}\sqrt{\frac{63}{143}}h_{3,3}^2, \quad (27)$$

$$h_{2,3}^2 = -\frac{1}{2}\frac{18}{\sqrt{143}}h_{3,3}^2, \quad (28)$$

$$h_{i,j}^l = h_{j,i}^l. \quad (29)$$

By this procedure one obtains a set of projector functions

$$P_k^l(r) = \sum_{i=1}^k \sum_{j=1}^k h_{i,j}^l p_{i,j}^l(r), \quad k = 1, 2, 3 \quad (30)$$

that satisfy the orthogonality relation

$$\int_0^\infty P_i^l(r) P_j^l(r) r^2 dr = 0 \quad \text{for } i \neq j. \quad (31)$$

Replacing $h_{i,j}^l$ by $k_{i,j}^l$ in eq.(20-29) gives the equations for the $k_{i,j}^l$. We found that the orthogonalization of the projectors improves the fitting procedure of our pseudopotential rather than keeping all $h_{i,j}^l$ zero for $i \neq j$ as was done in the former work of Goedecker *et al.*⁵ Treating the $h_{i,j}^l$ as independent pseudopotential parameters does not improve the results.

VII. SUMMARY

We developed a complete set of relativistic LDA pseudopotentials for the whole periodic system up to Rn. The pseudopotentials are easy to use as only a few parameters are necessary. All terms for both Fourier and real space are given analytically and no tabulated functions are needed. The pseudopotentials are highly accurate and transferable and have been tested in extensive atomic and molecular calculations.

Gaussian type pseudopotentials for other exchange correlation functionals or gradient corrected functionals can easily be constructed using our LDA parameter sets as an initial guess. The necessary programs are available from the authors upon request.

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TABLE I. LDA pseudopotential parameters. The meaning of the entries is given in the text.

H	1	.200000	-4.180237	.725075		.422738	5.906928	3.258196
He	2	.200000	-9.112023	1.698368		.484278	2.727013	.000000
Li	1	.787553	-1.892612	.286060			.000373	.014437
		.666375	1.858811		P	.430000	-6.654220	
		1.079306	-.005895			.389803	6.842136	3.856693
			.000019			.440796	3.282606	.000000
Li ^{sc}	3	.400000	-14.034868	9.553476	-1.766488	.084370		.002544
Be	2	.739009	-2.592951	.354839		S	.420000	-6.554492
		.528797	3.061666			.361757	7.905303	4.471698
		.658153	.092462			.405285	3.866579	.000000
			.000129				.005372	.022062
Be ^{sc}	4	.325000	-24.015041	17.204014	-3.326390	.165419	Cl	.410000
B	3	.433930	-5.578642	.804251			-6.864754	
		.373843	6.233928			.338208	9.062240	5.065682
		.360393	.000000			.376137	4.465876	.000000
			.000878				.010020	.025784
C	4	.348830	-8.513771	1.228432		Ar	.400000	-7.100000
		.304553	9.522842				.317381	10.249487
		.232677	.000000				.351619	4.978801
			.004104				.016395	.029171
N	5	.289179	-12.234820	1.766407		K	.950000	
		.256605	13.552243				.955364	.914612
		.270134	.000000				1.086411	.315462
			.003131					.068194
O	6	.247621	-16.580318	2.395701		K ^{sc}	.400000	-4.989348
		.221786	18.266917				.294826	11.238705
		.256829	.000000				.322359	5.256702
			.004476					.938947
F	7	.218525	-21.307361	3.072869		Ca	.2	.015795
		.195567	23.584942				.800000	.048923
		.174268	.000000				.669737	1.645014
			.015106				.946474	.585479
Ne	8	.190000	-27.692852	4.005906				.126329
		.179488	28.506098	-1.076245				.003362
		.214913	-.000090				.526550	.012779
			.010336					.000814
Na	1	.885509	-1.238867			Ca ^{sc}	.10	.390000
		.661104	1.847271	.582004				-4.928146
		.857119	.471133					.281909
			.002623					12.352340
Na ^{sc}	9	.246318	-7.545593	1.125997				.310345
		.141251	36.556987					5.722423
		.139668	-10.392083					.923591
			.038386					.021701
Mg	2	.651812	-2.864297			Sc ^{sc}	.11	.385000
		.556478	2.970957	1.329941				7.425036
		.677569	1.049881					.359707
			.005152					6.119585
Mg ^{sc}	10	.210950	-19.419008	2.871331				-2.563453
		.141547	40.316626					.243234
		.105469	-10.891113					6.376618
			.096277					.083053
Al	3	.450000	-8.491351					.093017
		.460104	5.088340	2.679700		Ti	.4	.720000
		.536744	2.193438	.000000				.528411
			.006154	.003947				1.866613
Si	4	.440000	-7.336103					1.440233
								3.658172
								.791146
								.967916
								.009333
								.025291
								.408712
								-4.826456
								.002010
								Ti ^{sc}
								.12
								.380000
								7.548789
								-.588377

.334235	6.925740	-3.142005		.259140	11.195226	-7.845825
.242416	5.079086	-6.284281		.251425	-.551464	-4.639237
	.122395	.057447			.207915	-.108249
.242947	-9.125896			.221665	-12.075354	
	.005822				.011475	
V 5	.690000			Ni 10	.560000	
	.514704	2.208670	1.896763	3.076377	.425399	3.619651
	.743504	1.115751	.286649		.584081	1.742220
		-.010973	.030816			-.020384
	.374890	-5.841633			.278113	-11.608428
		.002717				.008708
V ^{sc} 13	.375000	4.941291	-.096443	Ni ^{sc} 18	.350000	3.610311
	.326651	7.659390	-3.892229		.245105	12.161131
	.246407	4.256230	-5.941212		.234741	-.820624
		.156408	.008030			.269572
	.240792	-8.828518			.214950	-13.395062
		.006548				.013538
Cr 6	.660000			Cu 1	.580000	
	.498578	2.400756	2.072337	2.952179	.843283	.975787
	.719768	1.145557	.278236		1.089543	.024580
		-.013176	.035625			.010792
	.354341	-6.615878			1.291602	-.065292
		.003514				-.000730
Cr ^{sc} 14	.370000	5.113362	-.646819	Cu ^{sc} 11	.530000	
	.306011	8.617835	-4.137695		.423734	3.888050
	.241090	3.161588	-5.032906		.572177	1.751272
		.169781	.000411			-.024067
	.219577	-11.157868			.266143	-12.676957
		.009007				.010489
Mn 7	.640000			Zn 2	.570000	
	.481246	2.799031	2.486101	2.565630	.640712	2.088557
	.669304	1.368776	.316763		.967605	.163546
		-.013685	.042938			.012139
	.327763	-7.995418			1.330352	.010486
		.004536				.000225
Mn ^{sc} 15	.365000	6.748683	-.576569	Zn ^{sc} 12	.510000	
	.280753	9.379532	-5.575280		.400866	4.278710
	.254536	.371176	-4.229057		.539618	2.023884
		.164188	-.039396			-.025759
	.221422	-12.115385			.252151	-14.338368
		.009590				.012767
Fe 8	.610000			Ga 3	.560000	
	.454482	3.016640	2.583038	3.257635	.610791	2.369325
	.638903	1.499642	.326874		.704596	.746305
		-.014909	.049793			.029607
	.308732	-9.145354			.982580	.075437
		.005722				.001486
Fe ^{sc} 16	.360000	5.392507	-.030066	Ga ^{sc} 13	.490000	
	.269268	10.193723	-6.834982		.384713	4.831779
	.247686	.145613	-5.234954		.586130	1.940527
		.201450	-.075829			.026949
	.223021	-12.026941			.240803	-15.795675
		.010322				.015503
Co 9	.580000			Ge 4	.540000	
	.440457	3.334978	2.873150	3.091028	.493743	3.826891
	.610048	1.634005	.356083		.601064	1.362518
		-.017521	.058766			.043981
	.291661	-10.358800			.788369	.191205
		.007137				.002918
Co ^{sc} 17	.355000	3.418391	.482078	As 5	.520000	

.456400	4.560761	1.692389	-1.373804	.649998	1.739877	2.388208	1.205349
.550562	1.812247	-.646727		.874408	1.018294	.528223	
	.052466	.020562			-.057486	.104495	
.685283	.312373			.630668	-1.173911	.212179	
	.004273				.009380	-.011973	
Se 6	.510000			Zr ^{sc} 12	.470000	15.782342	.433648
	.432531	5.145131	2.052009		.396540	2.571767	-4.714509
	.472473	2.858806	-.590671		.388558	-.794123	-3.172114
		.062196	.064907			.301247	-.098654
	.613420	.434829			.520496	-1.548402	.826127
		.005784				.013187	-.010136
Br 7	.500000			Nb 5	.724000	4.021058	
	.428207	5.398837	1.820292		.699708	1.532651	1.428264
	.455323	3.108823	-.632202		.846672	.609675	.596788
		.074007	.068787			-.080816	.125243
	.557847	.555903			.516072	-2.696830	-1.694967
		.007144				.025653	-.031541
Kr 8	.500000			Nb ^{sc} 13	.460000	13.505394	.752434
	.410759	5.911194	1.967372		.393708	3.222025	-4.599342
	.430256	3.524357	-.691198		.403626	-.822037	-2.247366
		.087011	.086008			.246821	-.086659
	.517120	.629228			.513644	-1.489848	.823817
		.009267				.014064	-.012055
Rb 1	1.096207	.847333	-.748120	Mo 6	.699000	7.995868	
	.955699	.887460	.903088		.678126	1.289607	.998113
	1.156681	.461734	.336113		.800771	.301412	.741615
		-.043443	.057876			-.104124	.153906
	.664323	-1.362938			.453384	-2.809708	-6.820946
		.003708				.068972	-.075591
Rb ^{sc} 9	.490000	4.504151	-.741018	Mo ^{sc} 14	.430000	16.237452	1.496536
	.282301	9.536329	9.486634		.376255	3.362426	-5.289276
	.301886	2.209592	5.475249		.361734	-.379571	-4.067713
		-.867379	1.237532			.378681	-.124561
	.514895	.449376			.525828	-1.543211	1.074388
		.008685				.014460	-.014769
Sr 2	1.010000	.684749	-.062125	Tc 7	.673000	13.315381	
	.837564	1.200395	.926675		.677612	.819218	.348460
	1.174178	.439983	.018267		.784275	.028673	.658363
		.004022	.022207			-.080760	.140668
	.743175	-1.386990			.519890	-5.984224	.721822
		.002846				.026025	-.041776
Sr ^{sc} 10	.480000	5.571455	-1.079963	Tc ^{sc} 15	.430000	14.910011	1.046381
	.275441	9.995135	9.336679		.369721	3.917408	-5.268399
	.302243	3.169126	4.049231		.357772	-.270000	-3.737771
		-.576265	.990062			.340791	-.065948
	.502045	.438728			.510487	-1.586709	1.132307
		.008991				.015790	-.016485
Y 3	.900000	-.343891		Ru 8	.647214	8.687723	
	.782457	1.520655	1.484368		.625656	1.637866	1.329335
	.949864	.780950	.368739		.746425	.639012	.650376
		-.043336	.079989			-.095454	.164257
	.653851	-1.256930	-.075368		.440358	-4.883365	-3.063746
		.009198	-.011657			.046652	-.061808
Y ^{sc} 11	.475000	13.217914	1.353178	Ru ^{sc} 16	.430000	13.582571	.596227
	.414360	2.522621	-4.363769		.364084	4.480632	-5.268679
	.406442	-.569552	-3.020044		.364053	-.320372	-3.059714
		.251526	-.077005			.337322	-.103467
	.513304	-1.571003	.627616		.495850	-1.597870	1.165495
		.012450	-.007507			.017773	-.019725
Zr 4	750000	-.782611		Rb 9	.621429	5.397962	

		.524623	-.030901	.142077			.014666
	.626672	.328377			Tb ^{sc}	19	.514583
		.020900					.448694
	.299310	-18.269439					.424220
		.007193					.562400
Ce ^{sc}	12	.535000	18.847470	-.765636			-.008725
		.521790	1.321616	-1.700444			1.144007
		.470324	.972641	-1.451337	.000000	Dy ^{sc}	20
				.463710	.090257		.482809
							-.625802
			.703593	.074241			.051754
				.013265			.268260
			.306717	-17.214790			-22.911697
				.007568			.016197
Pr ^{sc}	13	.532083	18.424739	-.657669			
		.526850	1.012621	-1.717982			
		.458897	1.117060	-1.852109	.000000		
				.314280	.350982		.467229
			.747610	.017571			-.668924
				.010905			.058286
			.300773	-17.897119			.261670
				.008547			-23.922358
Nd ^{sc}	14	.529167	17.815030	-.594798			.017938
		.503000	1.529110	-2.153732		Ho ^{sc}	21
		.467013	.721553	-1.647499	.000000		.508750
				-.214396	1.100446		.432212
			.325290	-.543240			2.052797
				.611413			-3.674534
			.294743	-18.520228			.420138
				.009598			.253295
Pm ^{sc}	15	.526250	18.251723	-.492107			.895947
		.489879	1.308978	-2.507751			-.275149
		.472260	.160512	-1.565305	.000000		.205729
				-.339955	1.359017		
			.473709	-.429952			
				.064044			
			.291527	-19.305057		Er ^{sc}	22
				.010619			.17.105293
Sm ^{sc}	16	.523333	17.206792	-.532803			-.1.430953
		.479677	1.723635	-2.659367			.419948
		.490598	-.082403	-1.111009	.000000		2.144503
				-.240300	1.200867		.414455
			.470840	-.410630			-.2.294477
				.063352			.1.255135
			.284040	-19.984292			-.891960
				.011924			.749717
Eu ^{sc}	17	.520417	17.373516	-.648468		Tm ^{sc}	23
		.469043	1.763638	-2.916932			.502917
		.445907	.518046	-2.135186	.000000		17.247293
				.252258	.584324		-.1.627697
			.490038	-.426120			.413373
				.051028			1.947196
			.278401	-20.946528			-.409923
				.013267			.249126
Gd ^{sc}	18	.517500	17.512556	-.719534			
		.462014	1.551856	-3.068703			
		.456953	-.058347	-1.697711	.000000		
				.535540	.022024		.232629
			.482368	-.562601			
				.053128			
			.273390	-21.923490			
						Lu ^{sc}	25
							.497000
							17.037053
							-.1.661610
							.391206
							2.184678
							-.5.432346
							.393896
							-.7.23799
							.1.52450
							1.395416
							-.1.238744
Hf ^{sc}	12	.560000	5.134801	.529191			
		.422810	2.564442	-6.013732			
		.472681	-1.025275	-1.872548			
				.000000			

		.607504	-.331637	-.121021		.930121	-.379865	-.262716
	.426388	1.459363	-5.282764		.376428	.754315	-5.875580	
		.222119	-.121283			.219517	-.112145	
Ta 5	.744000	3.623116			Pt 10	.616000	11.027417	
	.581801	2.005338	3.027036			.520132	2.447430	2.640360
	.770646	.518567	1.185378			.658976	.408453	1.647716
		-.485635	.695148				-.763296	1.065883
	.534370	-2.202200	-1.666675			.451243	-4.552295	-2.102396
		.086716	-.094635				.146912	-.169306
Ta ^{sc} 13	.550000	4.546236	.779422		Pt ^{sc} 18	.500000	5.445832	1.156382
	.421853	2.708136	-5.790959	.947663		.409942	2.994366	-7.448772 4.243095
	.461345	-.724853	-2.215211	.000000		.398652	-.225181	-3.776974 .000000
		.649992	-.336371	-.101322			1.017060	-.348213 -.331919
	.410994	1.348495	-5.386947			.367964	.632067	-5.755431
		.205344	-.102353				.226472	-.114346
W 6	.719000	4.058450			Au 1	.650000	-1.963712	-1.698123
	.582463	2.161166	2.741500			.919308	1.539599	-.468779 -.792039
	.742307	.600973	1.299943			1.140351	.471229	-.497538 -.209758
		-.509800	.751739				.039349	.132970 -.153427
	.534959	-2.517063	-.789137		Au ^{sc} 11	.590000	11.604428	
		.075772	-.086193			.521180	2.538614	2.701113
W ^{sc} 14	.540000	4.800251	.901544			.630613	.394853	2.057831
	.418570	2.692204	-6.022637	1.218316				-.960055 1.296571
	.449555	-.702084	-2.451680	.000000		.440706	-4.719070	-1.650429
		.715480	-.385339	-.077093				.148484 -.169493
	.399602	1.177436	-5.553621		Hg 2	.640000	-3.296329	
		.205860	-.100046			.812108	1.765041	-.466127 -.799941
Re 7	.693000	8.180816				1.053714	.474056	-.531816
	.509816	2.269379	3.528529				.092330	-.001118
	.745839	.496693	.925829			1.100000	.120638	
		-.370589	.616765				.020931	
	.500954	-3.689630	-1.894601		Hg ^{sc} 12	.570000	2.134572	
		.111557	-.131595			.521802	3.293920	4.661001
Re ^{sc} 15	.530000	5.592660	.943957			.621648	2.100960	1.689988 .000000
	.403252	2.760720	-6.396415	.868732			.084989	.072771 .653348
	.440951	-.900546	-2.511211	.000000		.401894	-1.669886	-2.473265
		.788715	-.489984	-.017012			.155759	-.122282
	.390395	.875251	-5.672543		Tl 3	.630000	-1.235846	
		.209737	-.102862			.754005	1.875766	-.303680 -.781337
Os 8	.667000	9.440459				.903742	.759668	-.586721
	.510307	2.402367	3.046706				.168641	.004459
	.717553	.499523	1.053284			1.063512	.247614	
		-.430746	.701752				.022941	
	.487586	-4.142035	-1.666100		Tl ^{sc} 13	.550000	7.301886	
		.116941	-.139761			.502423	3.326560	4.341390
Os ^{sc} 16	.520000	5.613073	.921955				.572016	1.272807 2.992206 .000000
	.410578	2.785758	-6.692130	2.247034				.012233 .031664 1.019164
	.422395	-.590006	-3.018323	.000000			.393185	-3.200652 -3.008296
		.870817	-.412886	-.139506				.186849 -.170651
	.380252	.880133	-5.732892		Pb 4	.617500	.753143	
		.216440	-.103221			.705259	1.979927	-.164960 -.806060
Ir 9	.641000	10.720016				.846641	.864420	-.540969
	.509960	2.445999	2.811037				.207711	.012948
	.684971	.461792	1.304726			.971939	.374967	
		-.565347	.859620				.029256	
	.471745	-4.545484	-1.635428		Bi 5	.605000	6.679437	
		.127199	-.151950			.678858	1.377634	-.513697 -.471028
Ir ^{sc} 17	.510000	4.904509	1.313786			.798673	.655578	-.402932
	.404469	3.243278	-7.315509	2.956978			.305314	-.023134
	.411426	-.380574	-3.504403	.000000		.934683	.378476	

			.029217	
Po	6	.592500	10.411731	
		.647950	1.144203	-.735851 -.339386
		.748947	.594562	-.353595
			.396354	-.031462
		.880468	.433232	
			.033886	
At	7	.580000	13.520411	
		.627827	.945557	-.965903 -.190429
		.709823	.527078	-.318821
			.480774	-.034954
		.838365	.468948	
			.037544	
Rn	8	.570000	14.629185	
		.615182	.981832	-1.038963 -.120456
		.676697	.612279	-.344122
			.549896	-.023760
		.788337	.557746	
			.045488	

TABLE II. Comparison of bond lengths of molecules calculated with our pseudopotentials (PSP) and obtained with GAUSSIAN 94 or NUMOL²¹ (AE) and the experimental data. All GAUSSIAN 94 calculations were done with a 6-311++G(3df,3pd) basis set if not otherwise mentioned. Bond lengths are given in Bohr.

Molecule	PSP	AE	Expt.	Ref.
H ₂	1.447	1.447	1.401	22
Li ₂	5.100 ^{sc} , 5.016	5.120	5.051	22
LiH	3.029 ^{sc} , 2.929	3.029	3.015	22
Be ₂	4.516 ^{sc} , 4.497	4.510	4.63	23
BF ₃	2.477	2.469	2.470	24
BH	2.363	2.371	2.373	22
CH ₄	2.072	2.072	2.052	25
C ₂ H ₂	r(CC)	2.263	2.270	2.274
	r(HC)	2.028	2.030	2.005
N ₂		2.067	2.070	2.074
NH ₃		1.932	1.932	1.912
HCN	r(CN)	2.169	2.174	2.179
	r(HC)	2.038	2.039	2.013
H ₂ O		1.836	1.834	1.809
CO		2.127	2.130	2.132
CO ₂		2.196	2.195	2.192
F ₂		2.622	2.613	2.668
HF		1.764	1.760	1.733
CH ₃ F	r(CF)	2.605	2.592	2.612
	r(HC)	2.082	2.082	2.069
Na ₂		5.76	5.64	5.818
NaH		3.534 ^{sc} , 3.381	3.529	3.566
Mg ₂		6.31	6.41	7.351
MgH		3.318 ^{sc} , 3.279	3.313	3.271
AlH		3.140	3.174	3.169
SiH ₄		2.808	2.820	2.795
SiO		2.827	2.861	2.853
SiF ₄		2.922	2.952	2.936
P ₂		3.547	3.542	3.578
PH ₃		2.696	2.704	2.671
PN		2.789	2.808	2.871
S ₃		3.595	3.609 ^a	
H ₂ S		2.553	2.558	2.524
CS		2.882	2.897	2.901
CS ₂		2.918	2.930	2.934
Cl ₂		3.725	3.742	3.756
HCl		2.436	2.440	2.409
CH ₃ Cl	r(CCl)	3.330	3.331	3.374
	r(CH)	2.072	2.072	2.060
K ₂		6.936	7.358 ^a	7.413
KH		2.200 ^{sc} , 2.969	2.303 ^a	2.307
CaH		3.706 ^{sc} , 3.187	4.126 ^a	3.783
ScH		3.304 ^{sc} , 3.182	3.300 ^b	
ScO		3.116 ^{sc}	3.109 ^b	3.152
TiO		3.018 ^{sc} , 2.840	3.020 ^b	3.062
VO		2.943 ^{sc} , 2.845	2.959 ^b	3.003
CrO		2.955 ^{sc} , 2.903	2.997 ^b	3.052
MnO		2.996 ^{sc} , 2.991	3.032 ^b	3.114
FeO		2.958	2.994 ^b	2.97
CoO		2.932	3.037 ^b	3.024
NiO		3.027	3.035 ^b	
NiH		2.726		2.787
CuO		3.153 ^{sc} , 2.749	3.176 ^b	3.258

CuH	2.731 ^{sc} , 2.463	2.755 ^b	2.765	22
Cu ₂	4.086 ^{sc} , 3.472	4.110 ^b	4.195	22
ZnO	3.157 ^{sc} , 2.886	3.161 ^b		
ZnH	3.010 ^{sc} , 2.858	3.025 ^b	3.013	22
GaH	3.176 ^{sc} , 3.095	3.173	3.143	22
GaO	3.167 ^{sc} , 3.022	3.173		
GaF	3.376 ^{sc} , 3.183	3.367	3.353	31
GeH ₄	2.861	2.896	2.882	24
GeO	3.010	3.074	3.118	22
As ₂	3.912	3.951	3.974	22
As ₄	4.551	4.573	4.602	24
AsH ₃	2.875	2.887	2.855	24
H ₂ Se	2.783	2.788	2.759	24
Se ₂	4.089	4.097	4.076	22
Se ₃ (C _{2v})	4.142	4.146		
SeO ₂	3.041	3.045	3.038	31
Br ₂	4.296	4.299	4.314	22
HBr	2.701	2.705	2.670	22
CH ₃ Br r(CH)	2.069	2.063	2.052	24
r(CBr)	3.636	3.635	3.653	24
BrF	3.326	3.322	3.318	22
BrF ₃ r ₁ (BrF)	3.437	3.434	3.420	24
r ₂ (BrF)	3.289	3.285	3.252	
Rb ₂	7.671 ^{sc} , 7.333		7.956	32
RbH	4.368 ^{sc} , 3.072		4.473	22
SrH	4.009 ^{sc} , 3.522		4.053	22
SrI ₂	5.560 ^{sc} , 5.327		5.69	24
SrO	3.591 ^{sc}		3.630	22
ZrO	3.235 ^{sc} , 2.848		3.234	22
RhC	3.027		3.049	22
PdH	2.865		2.889	
AgH	3.023 ^{sc} , 2.688		3.056	22
Ag ₂	4.717 ^{sc} , 3.760		4.67	22
CdH	3.323 ^{sc} , 3.108		3.329	22
InH	3.504 ^{sc} , 3.394	3.512 ^c	3.473	22
SnH	3.331		3.373	22
SnO	3.401		3.473	22
SnS	4.123		4.174	22
Sb ₂	4.624		4.70	33
SbCl ₃	4.414		4.411	34
Te ₂	4.824		4.832	22
H ₂ Te	3.146	3.156 ^c	3.133	24
HI	3.073	3.073 ^c	3.031	22
I ₂	5.029		5.039	22
Cs ₂	8.479 ^{sc} , 7.976		8.783	35
CsH	4.630 ^{sc} , 3.171		4.713	22
BaH	4.176 ^{sc} , 3.403		4.217	22
IrC	3.324		3.180	22
PtH	2.872		2.888	22
PtC	3.612		3.371	22
AuH	2.898 ^{sc} , 2.424		2.879	22
HgH	3.278 ^{sc} , 3.067		3.284	22
TlH	3.600 ^{sc} , 3.440		3.534	22
TlCl	4.472		4.81	22
PbH	3.433		3.475	22
PbS	4.237		4.526	22
PbCl ₂	4.552		4.609	34
BiH	3.374		3.411	22

^a: GAUSSIAN 94 with 3-21G basis set

^b: GAUSSIAN 94 with 6-311++G(3d,3pd) basis set

^c: calculated with NUMOL

TABLE III. Transferability errors

Element	state	ΔE (Ha)	Error (Ha)
C	2s ¹ 2p ³ 3d ⁰	0.3073	-0.40×10 ⁻³
	2s ² 2p ³ 3d ⁰	0.4294×10 ⁻¹	0.11×10 ⁻³
	2s ² 2p ¹ 3d ⁰	0.3612	-0.44×10 ⁻³
	2s ² 2p ² 3d ¹	0.3882	0.95×10 ⁻⁴
	3s ¹ 3p ³ 3d ⁰	0.2529	-0.20×10 ⁻³
	3s ² 3p ³ 3d ⁰	-0.5293×10 ⁻²	0.38×10 ⁻⁴
	3s ² 3p ¹ 3d ⁰	0.2673	-0.28×10 ⁻³
	3s ² 3p ² 3d ¹	0.2462	0.43×10 ⁻⁴
	4s ¹ 4p ³ 4d ⁰	0.2970	-0.48×10 ⁻³
	4s ² 4p ³ 4d ⁰	-0.1682×10 ⁻¹	0.58×10 ⁻⁴
Si	4s ² 4p ¹ 4d ⁰	0.2681	-0.23×10 ⁻³
	4s ² 4p ² 4d ¹	0.1879	0.52×10 ⁻⁴
	5s ¹ 5p ³ 5d ⁰	0.2605	-0.40×10 ⁻³
	5s ² 5p ³ 5d ⁰	-0.2482×10 ⁻¹	0.46×10 ⁻⁴
	5s ² 5p ¹ 5d ⁰	0.2510	-0.35×10 ⁻³
Ge	5s ² 5p ² 5d ¹	0.1084	0.34×10 ⁻⁴
	6s ¹ 6p ³ 6d ⁰	0.3181	-0.35×10 ⁻³
	6s ² 6p ³ 6d ⁰	-0.3587×10 ⁻¹	-0.41×10 ⁻⁵
	6s ² 6p ¹ 6d ⁰	0.2505	-0.46×10 ⁻³
	6s ² 6p ² 6d ¹	0.7216×10 ⁻¹	0.33×10 ⁻⁴
Ti	4s ¹ 4p ¹ 3d ²	0.1198	-0.17×10 ⁻³
	4s ² 4p ⁰ 3d ⁰	0.1166×10 ¹	-0.47×10 ⁻¹
	4s ⁰ 4p ⁰ 3d ⁰	0.3258×10 ¹	-0.10
	4s ² 4p ¹ 3d ²	0.3593×10 ⁻¹	0.65×10 ⁻⁴
	4s ¹ 4p ¹ 3d ²	0.1198	-0.37×10 ⁻⁴
Ti ^{sc}	4s ² 4p ⁰ 3d ⁰	0.1166×10 ¹	-0.31×10 ⁻²
	4s ⁰ 4p ⁰ 3d ⁰	0.3258×10 ¹	-0.28×10 ⁻²
	4s ² 4p ¹ 3d ²	0.3593×10 ⁻¹	0.15×10 ⁻³

FIG. 1. Relativistic all-electron (solid) and pseudo (dashed) wave functions of the valence electrons of gold. The difference between them is shown by the dotted line on a logarithmic scale.

Figure 1: Relativistic all-electron (solid) and pseudo (dash) wave functions for the valence states of gold. The difference between them is shown by the dotted line on a logarithmic scale.



